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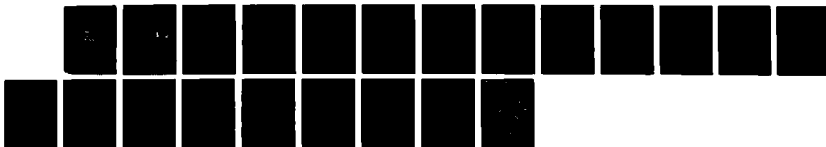
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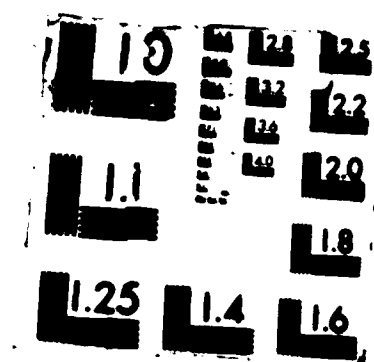
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Formation and Decomposition of Sulfur Compounds in Dispenser Cathodes

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1. INTRODUCTION

During operation of dispenser cathodes, sulfur is often observed on the cathode surfaces. Sulfur has been identified as a poison in dispenser cathodes.^{*} Thus, the sources of sulfur must be identified and eliminated to ensure uniform, high-emission current density in high-reliability cathodes for space applications.

A dispenser cathode consists of a porous tungsten matrix filled with a barium calcium aluminate impregnant. During operation at about 1100°C, barium is formed by the reaction of the impregnant with the tungsten matrix. A constant supply of barium and oxygen replenishes material lost from the emitting surface by evaporation and maintains low-work-function barium-on-oxygen dipoles on the cathode surface. During operation, compounds of sulfur in the cathode release sulfur that can displace oxygen on the surface and increase the work function.

Sulfur can be introduced into the cathode from the starting materials, from the tube environment, or during processing. Recent use of high-purity starting materials has reduced to an insignificant level the amount of sulfur introduced into the cathode from the starting materials. However, sulfur contamination can still occur during any high-temperature processing step in which cathodes are heated in dry hydrogen in the presence of sulfur-containing materials (such as stainless steel). Under such conditions, hydrogen sulfide, H_2S , is formed and is transported to the cathode impregnant. Hydrogen sulfide reacts with the cathode impregnant, forming barium and calcium sulfide compounds and chemically stable barium aluminate. When contaminated cathodes are activated, the sulfides are converted to sulfur, which alters the surface dipole and increases work function.

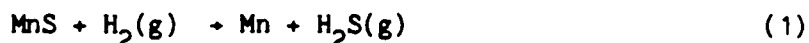
^{*}J. Cronin, "Practical Aspects of Modern Dispenser Cathodes," Microwave J. (September 1979).

In this report, I use thermodynamic data to examine two steps in the sulfur contamination process: sulfur compound formation during cathode manufacture and processing, and sulfur compound decomposition in the cathode during activation and operation. The details of those chemical reactions are presented in the Appendix.

II. GENERATION OF HYDROGEN SULFIDE FROM STAINLESS STEEL

The first step in sulfur contamination of dispenser cathodes in a furnace or tube environment is the generation of a volatile sulfur compound. As an example, assume that 304 stainless steel is present in the furnace.

Stainless steel, when heated to high temperature in hydrogen, can evolve hydrogen sulfide from a reaction of hydrogen with sulfide compounds. For example, stable sulfur compounds in the steel, such as manganese sulfide, can be converted to H_2S gas by the following reaction:



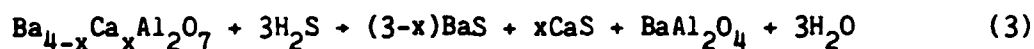
As shown in the Appendix, the hydrogen sulfide vapor pressure for this reaction is

$$p(H_2S) = 5 \times 10^{-6} \text{ atm or } 4 \times 10^{-3} \text{ Torr} \quad (2)$$

for a furnace temperature of 1500 K (1227°C) and a hydrogen pressure of 1 atm (760 Torr). Thus, a significant amount of H_2S is formed and can be transported to the cathode. Reactions of H_2S with the impregnant in dispenser cathodes are examined in the next section.

III. SULFIDE FORMATION

In the second step of sulfur contamination, the cathode impregnant reacts with hydrogen sulfide to form sulfide compounds. The relatively high concentration of H_2S in the contaminated furnace atmosphere favors formation of barium and calcium sulfides. Those sulfides decompose during cathode operation in vacuum, causing sulfur contamination. An analysis of thermodynamic data, in the Appendix, indicates that H_2S reacts with the impregnant to form barium sulfide and calcium sulfide, although sulfate formation is unlikely. Furthermore, the reaction of hydrogen sulfide with the barium calcium aluminate solid solutions in the impregnant forms nonemissive barium aluminate. For example:



Thus, reactions of the impregnant with H_2S produce two adverse effects: (1) incorporation of sulfur in the impregnant, which is known to degrade cathode performance; and (2) depletion of active (volatile) barium required for cathode operation.

IV. GENERATION OF SULFUR DURING CATHODE OPERATION

The final step in the poisoning mechanism is the generation of sulfur from the sulfides. The presence of sulfides in the impregnant poisons dispenser cathodes during activation and operation. When a sulfide-contaminated cathode is heated, the barium and calcium sulfides decompose and act as a source of barium, calcium, and sulfur according to the following reactions:



The dynamic equilibrium between the generation of sulfur from the decomposition of sulfides (estimated in Fig. 1) and desorption from the emitting surface determines the dynamics of sulfur coverage of the emitting surface. It can be used to understand the dynamics of cathode emission degradation after hot shotting. When the cathode temperature is increased, sulfur is desorbed from the surface and cathode emission increases. When the cathode temperature is reduced to the operating temperature, the sulfur desorption rate decreases, the surface coverage of sulfur increases, and emission current falls--behavior that is the signature of sulfide contamination of the impregnant.

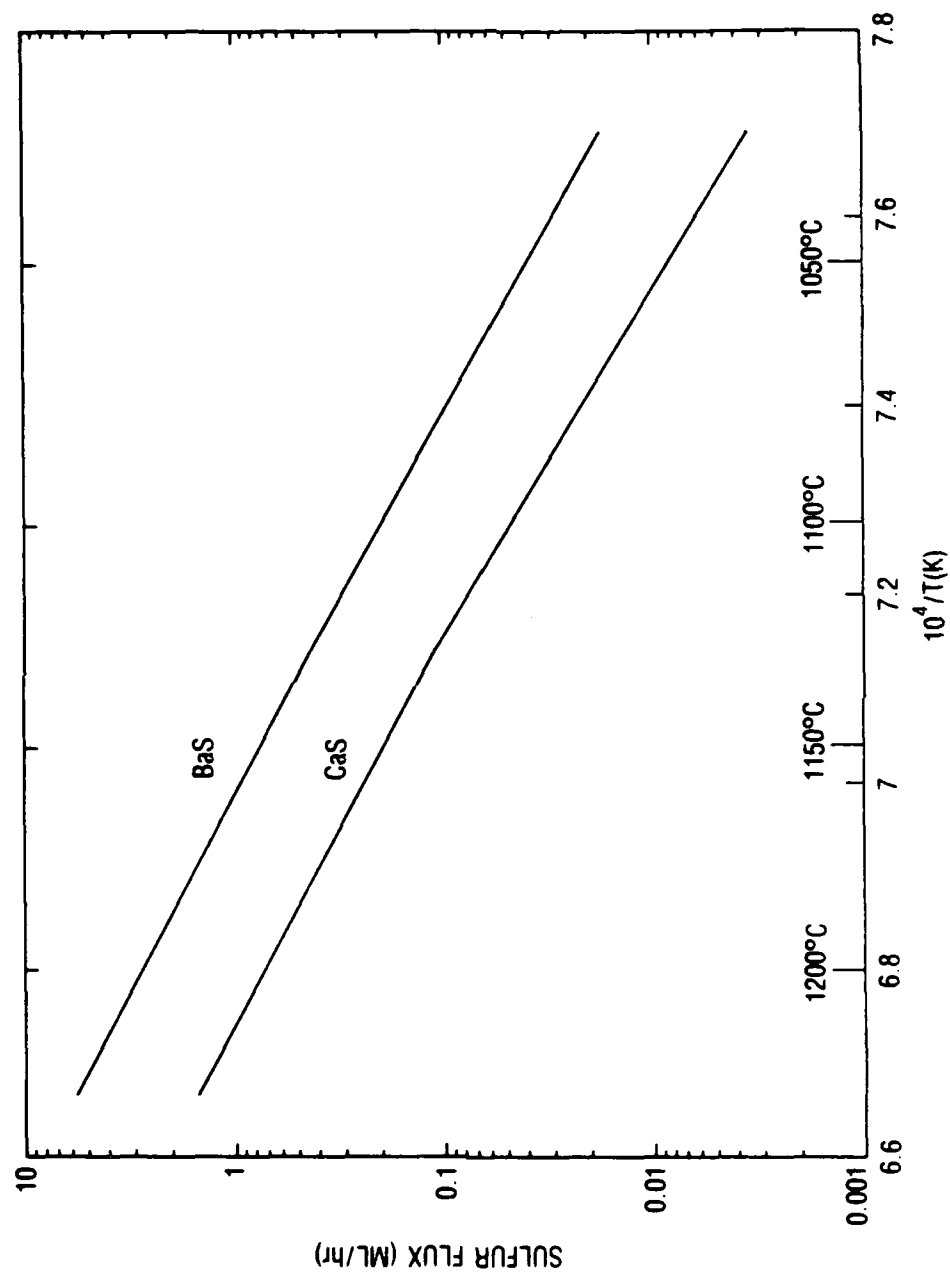


Fig. 1. Sulfur flux from contaminated cathodes.

V. SUMMARY AND CONCLUSIONS

On the basis of thermodynamic analysis, the fate of sulfur in dispenser cathodes can be predicted. The following are the major conclusions:

1. Sulfur can be accumulated in the impregnant by sulfides formed at high temperature in the presence of high hydrogen sulfide vapor pressure derived from sulfide-containing materials, such as stainless steel.
2. During activation and operation, sulfur is generated from the sulfides in the impregnant. Sulfur can accumulate on the cathode surface at low cathode operating temperatures and leads to emission current degradation.
3. Inert barium aluminate is also formed when the impregnant is exposed to hydrogen sulfide and reduces the supply of barium to the cathode surface.
4. Based on these reactions, sulfide-containing materials such as stainless steel should not be used in a hydrogen atmosphere for high-temperature processing of dispenser cathodes.

APPENDIX: THERMODYNAMICS OF CATHODE SULFIDE CHEMISTRY

In this appendix, the formation and stability of sulfides and sulfates in the impregnant are estimated using thermodynamic data. The kinetics of sulfur contamination are sensitive to the structure of the cathode and furnace, which are poorly characterized in typical use. For this reason, the plausibility of contamination is shown here but the detailed kinetics are beyond the scope of this report.

A.1. GENERATION OF HYDROGEN SULFIDE FROM STAINLESS STEEL

Sulfur contamination of the impregnant can occur through exposure of the cathode to sulfur-containing fixtures during firing operations. When stainless-steel fixtures (e.g., type 304) are used in a hydrogen furnace, sulfides in the steel can be converted to hydrogen sulfide, H_2S . The concentration of sulfur and other elements in stainless steel is summarized in Table A-1. We will assume that equilibrium conditions have been achieved in the steel and that sulfur exists as the most chemically stable compound, identified using the data in Table A-2. As shown in the table, manganese sulfide, MnS , has the lowest Gibbs free energy of possible sulfides in stainless steel. Exposure of stainless steel to dry hydrogen reduces the manganese sulfide according to the following reaction and Gibbs (free) energy, G_r , at 1500 K (1227°C):



$$\begin{aligned} G_r &= -(-56.8) - (0) + (0) + (-20.38) \\ &= 36.4 \text{ kcal/mol} \end{aligned}$$

The Gibbs energies used in this report were calculated from the standard enthalpies and entropies taken from Kubaschewski and Alcock. The Gibbs energy is given by*

*O. Kubaschewski and C. B. Alcock, Metallurgical Thermochemistry, 5th ed., Pergamon Press, Oxford, England (1979).

TABLE A-1. CHEMICAL COMPOSITION OF 304 STAINLESS STEEL

Element	Concentration, mol%
Metals	
Ni	10
Si	1
Fe	67.5
Cr	19
Mn	2
Nonmetals	
C	0.8
P	0.045
S	0.030

SOURCE: R. C. Weast, ed., Handbook of Chemistry and Physics, The Chemical Rubber Company (1970), p. F-127.

TABLE A-2. STABILITY OF SULFIDES IN STAINLESS STEEL

Compound	Gibbs Free Energy, kcal/mol of S
MnS	-56.79 (Most stable species)
CrS	-40.19
Cr ₂ S ₃	-29.71
Mo ₂ S ₃	-27.97
MoS ₂	-27.65
MnS ₂	-27.48
SiS ₂	-25.10
FeS	-24.40
Ni ₃ S ₂	-22.37
NiS	-20.22
FeS ₂	-13.79

SOURCE: O. Kubaschewski and C. B. Alcock, Metallurgical Thermochemistry, 5th ed., Pergamon Press, Oxford, England (1979).

$$G = H + TS \quad (A-2)$$

where H is the standard enthalpy of formation of the compound from the elements, S is the third-law entropy at 298°C minus the entropies of the component elements, and T is the temperature of the reaction. No correction was made for the change in heat capacity with temperature. G_f can be used to estimate the equilibrium pressure of H_2S by calculating the equilibrium constant from

$$\begin{aligned} K &= p(H_2S)/p(H_2) = e^{-[G/RT]} \\ &= 5 \times 10^{-6} \end{aligned} \quad (A-3)$$

where R is the ideal gas constant (1.9872 cal/deg-mol), T is the furnace temperature, assumed to be 1500 K (or 1227°C), and the activity of the solid phases has been set equal to 1. If the hydrogen pressure is 1 atm, then the pressure of H_2S will be

$$p(H_2S) = 5 \times 10^{-6} \text{ atm} = 4 \times 10^{-3} \text{ Torr} \quad (A-4)$$

Thus, reduction of sulfides provides the H_2S for vapor transport to the cathode.

A.2. FORMATION OF SULFIDES AND SULFATES IN CATHODE IMPREGNANTS

Hydrogen sulfide that impinges on the cathode reacts with the cathode impregnant to form sulfur-containing compounds. The flux of the potential cathode contaminants from the stainless steel can be estimated using the expression for Langmuir evaporation:

$$dm(M_i)/dt = 44.3p_i(MW_i/T)^{1/2} \quad (A-5)$$

where $dm(M_1)/dt$ is the mass evaporation rate in grams per square centimeter second ($g/cm^2\text{-sec}$) for species M_1 , MW_1 is the molecular weight, and T is the temperature of the steel. The H_2S pressure in Eq. (A-4) was used to estimate a hydrogen sulfide flux of 1×10^{-6} mol/sec- cm^2 . As a worst case consider the reaction of hydrogen sulfide with barium oxide as in a 4:1:1 ($BaO:CaO:Al_2O_3$ mole ratio) impregnant:



$$\begin{aligned} G_r &= -(-98.4) - (-20.38) + (-100.24) + (-41.9) \\ &= -23.4 \text{ kcal/mol} \end{aligned}$$

This negative Gibbs energy indicates that the reaction occurs in the direction shown. The reaction's equilibrium constant is

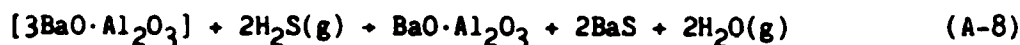
$$K = p(H_2O)/p(H_2S) = 3 \times 10^3$$

For the H_2S pressure in Eq. (A-4), the equilibrium water vapor pressure is

$$p(H_2O) = 10 \text{ Torr} \quad (A-7)$$

For a hydrogen atmosphere that has a partial pressure of water lower than 10 Torr, BaS and water will be formed according to the reaction in Eq. (A-6). For water vapor pressures higher than 10 Torr, BaS in the impregnant will react to form H_2S and BaO.

Impregnants (e.g., 5:3:2) that do not contain a barium oxide phase will also form sulfides during exposure to hydrogen sulfide. To model sulfide formation in these more stable impregnants, we consider the following reaction:



$$\begin{aligned} G_r &= -(-628.9) - 2(-20.38) + (-411.0) + 2(-100.2) + 2(-41.89) \\ &= -25.5 \text{ kcal/mol} \end{aligned}$$

The equilibrium constant is given by

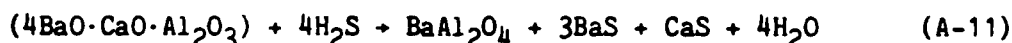
$$K = [p(\text{H}_2\text{O})/p(\text{H}_2\text{S})]^2 = 5 \times 10^3 \quad (\text{A-9})$$

The vapor pressure of water, based on Eq. (A-9) and on the H_2S vapor pressure from Eq. (A-4), is

$$p(\text{H}_2\text{O}) = 3 \times 10^{-1} \text{ Torr} \quad (\text{A-10})$$

In this case, and for the even more stable barium calcium aluminate solid solutions, the formation of sulfides is less favored than for barium oxide and will require even lower water pressures.

An upper limit for the rate of sulfide formation can be estimated for the reaction of a barium-oxide-containing impregnant with hydrogen sulfide. The actual accumulation rate of sulfur in the impregnant will be decreased by the existence of less reactive phases in most impregnants and transport into and out of the pores. Assuming that the arrival of H_2S calculated using Eq. (A-5) is rate limiting, the rate of BaS accumulation from the reaction in Eq. (A-6) will be about $1 \times 10^{-6} \text{ mol/cm}^2\text{-sec}$. Assuming that the cathode is 1.2 cm in diameter (surface area of about 1 cm^2) and is 1 mm thick and 80% dense, the impregnant will weigh 0.08 g for a density of about 4 g/cm^3 . For a 4:1:1 impregnant with a formula weight of 771.4 g/mol, there will be about 1×10^{-4} mol of impregnant, the amount of sulfide produced according to the reaction

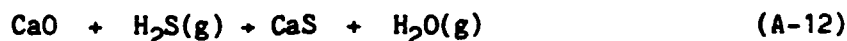


Thus, 4 mol of H_2S is required for each mole of impregnant. Based on the BaS accumulation rate above, about 7 min and 4×10^{-4} mol of H_2S will be required to fully convert the impregnant in the cathode to sulfides and barium aluminate. Because firing times on the order of 5 to 10 min are often used, a large fraction of the impregnant potentially will be converted to sulfides. Thus, the reaction of the impregnant with hydrogen sulfide from steel results in

major contamination of the cathode impregnant and surface contamination by sulfur during operation.

A.3. FORMATION OF CALCIUM SULFIDE

Calcium oxide is a pure phase component in most impregnant compositions. It can react with hydrogen sulfide to form calcium sulfide as follows:



$$\begin{aligned} G_r &= -(-114.2) - (-20.38) + (-107.7) + (-41.9) \\ &= -15.0 \text{ kcal/mol} \end{aligned}$$

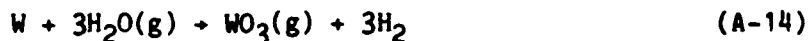
The equilibrium water pressure is

$$p(\text{H}_2\text{O}) = 6 \times 10^{-1} \text{ Torr} \quad (\text{A-13})$$

Because this water vapor pressure is high, CaS is expected to be formed in most cathode impregnants under dry conditions in the presence of H_2S .

A.4. FIRING IN WET HYDROGEN

Using wet hydrogen gas may prevent the formation of sulfides from hydrogen sulfide. However, as explained in this section, that procedure can oxidize the tungsten. Whether such oxidation reactions occur will depend on kinetics, which must be determined experimentally under the actual conditions in the furnace. For $p(\text{H}_2\text{O})$ greater than 0.15 Torr, oxidation of the tungsten can occur by



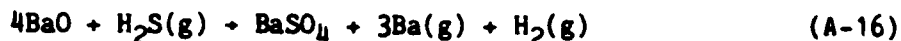
Thus, the water vapor pressure to suppress H_2S formation in Eqs. (A-10) and (A-13) is higher than the pressure to oxidize tungsten, and some tungsten oxide will be formed. Tungsten trioxide reacts with the impregnant to form tungstates of barium and calcium, as illustrated by



The presence of tungstates can disrupt barium transport, resulting in difficult activation and shorter cathode life. Thus, the best procedure for avoiding sulfur contamination is to use dry hydrogen in a sulfur-free environment.

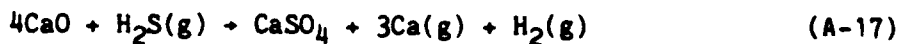
A.5. FORMATION OF SULFATES

In this section, we show that sulfates are unlikely to form from hydrogen sulfide. The following reactions can be written for the reduction of barium and calcium sulfates by H_2S :



$$\begin{aligned} G_r &= -4(-98.4) - (-20.38) + (-218.7) + 3(4.89) + (0) \\ &= 210 \text{ kcal/mol} \end{aligned}$$

and



$$\begin{aligned} G_r &= -4(-114.2) - (-20.38) + (-207.7) + 3(2.04) + (0) \\ &= 275.6 \text{ kcal/mol} \end{aligned}$$

Both reactions have very high positive free energies and will not occur in the cathode. The equilibrium constants are given by

$$\begin{aligned} K &= p^3(\text{Ba})[p(\text{H}_2)/p(\text{H}_2\text{S})] \\ &= 2 \times 10^{-31} \end{aligned} \quad (\text{A-18})$$

and

$$\begin{aligned} K &= p^3(\text{Ca})[p(\text{H}_2)/p(\text{H}_2\text{S})] \\ &= 7 \times 10^{-41} \end{aligned} \quad (\text{A-19})$$

For $p(\text{H}_2\text{S}) = 3.5 \times 10^{-4}$ Torr and $p(\text{H}_2) = 1$ atm, the metal pressures will be $p(\text{Ba}) = 8 \times 10^{-10}$ Torr and $p(\text{Ca}) = 5 \times 10^{-13}$ Torr. Because the evaporation rate of the metals is proportional to their vapor pressure, very little barium and calcium will be made by reaction with H_2S and very little sulfate will be formed.

A.6. CONTAMINATION OF THE EMITTING SURFACE

Sulfur contamination of the emitting surface can occur during activation and operation through the generation of sulfur from barium and calcium sulfides formed in the impregnant. Those reactions for the thermal decomposition of barium sulfide and calcium sulfide can be written as



and



The equilibrium constant for the decomposition of barium sulfide (and a similar expression for calcium sulfide) is

$$K = p(\text{Ba}) p(\text{S}) \quad (\text{A-21})$$

Assuming that the barium and sulfur vapor pressures are equal, we calculated the vapor pressures and equilibrium constants and list them in Table A-3.

During cathode activation and operation, the sulfur flux from the pores is determined by the vapor pressures in Table A-3, the temperature, T , and molecular weight, MW , by

$$[dL(\text{monolayers})/dt(\text{hr})] = 1.3 \times 10^{11} p(\text{Torr}) [MW(\text{g/mol}) T(\text{K})]^{-1/2} \quad (\text{A-22})$$

TABLE A-3. DECOMPOSITION OF BARIUM AND CALCIUM SULFIDES

Compound	Temperature, K	Gibbs Energy	Equilibrium Constant	Pressure, Torr
BaS	1300	135.04	2×10^{-23}	3×10^{-9}
	1400	128.82	8×10^{-21}	7×10^{-8}
	1500	122.63	1×10^{-18}	9×10^{-7}
CaS	1300	139.95	4×10^{-24}	1×10^{-9}
	1400	133.58	1×10^{-21}	3×10^{-8}
	1500	127.24	3×10^{-19}	4×10^{-7}

We have assumed that there are 10^{15} atoms/cm² in a monolayer. If the cathode has 20% porosity, then the maximum possible rate of surface coverage normalized to the surface area of the cathode will be one-fifth the rate from the pores in Eq. (A-22). The sulfur surface coverage will also be reduced by evaporation from the surface and the pore. The rate of surface coverage in Fig. 1 was calculated using one-fifth the value from Eq. (A-22). The actual surface coverage will be lower than that calculated by integrating the data in Fig. 1 because of sulfur loss by pore and surface evaporation. According to the discounted calculation, the supply rate can vary by a factor of 3, depending on whether BaS or CaS is the decomposing species. BaS is probably formed in more active impregnants such as BaO:CaO:Al₂O₃ = 4:1:1, and CaS is formed in more stable impregnants such as 5:3:2.

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